

POPLAR CREEK

FISH SAMPLING DATA

SPECIAL SAMPLING PROGRAM

1982 ONLY

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Document: # Unnumbered; Date 10/8/82;

Title/Subject Ltr., AC Stiff to M Mitchell, "Poplar  
Creek Fish Analysis Program for the . . ." 6pp

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## NUCLEAR DIVISION

INTERNAL CORRESPONDENCE

October 8, 1982

K/TL/AT-174

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Poplar Creek Fish Analysis Program for the Determination of Methylmercury, Polychlorinated Biphenyls (PCBs), and Uranium

The results from the fish analysis program are presented in Table 1. The data for PCBs determined as the 1260 Aroclor, indicate very low concentrations are present in almost all samples. Uranium concentrations are also very low. The methylmercury results, expressed as  $\mu\text{g/g}$  of Hg in fish, are significant (greater than or equal to  $0.5 \mu\text{g Hg/g}$  fish) in 18% of the samples.

Environmental and Effluent Analysis Procedure EC440<sup>(1)</sup> was used for PCB determination. Two- to five-gram samples were digested in methanolic potassium hydroxide and extracted with diethyl ether. The ether was taken to dryness under nitrogen and the residue redissolved in hexane. The resulting solution was analyzed by gas chromatography. The chromatograms showed a pattern of peaks most consistent with Aroclor 1260 and were quantitated as such based on a six-peak identification. The U.S. Environmental Protection Agency (EPA) control for PCBs in fish (concentrate No. 1) was used in developing the method and as a control throughout the program. The use of this control demonstrated the method's ability to separate and recover PCBs from fish. Results from 12 replicate analysis of the EPA control are presented in Table 2. Our results for this standard are biased high by approximately  $0.5 \mu\text{g}$  1260/g fish. This is probably due to the presence of Aroclor 1254 which was not taken into account but has overlapping peaks.<sup>(2)</sup> The samples taken from Poplar Creek may also contain traces of the 1254 Aroclor. In spite of this high bias, the results are well below the FDA limit of 5 ppm.<sup>(3)</sup> The detection limit of  $0.1 \mu\text{g/g}$  for PCBs in fish based on a 3 g sample has been set. The precision of the method at the 95% confidence limit is  $\pm 0.3 \mu\text{g}$  PCB per gram of fish, at EPA reference standard levels.

The method for uranium determination in fish was based on tri-n-octylphosphineoxide (TOPO) extraction followed by fluorimetric detection. In order to conserve time and sample preparation on aliquot from the PCB digest was taken for uranium determination. The sample is acidified with nitric acid and extracted with TOPO. An aliquot of the extract is removed for fusion followed by fluorescence detection. This extraction-fluorimetric procedure is similar to Environmental Analysis Procedures EC 370 and EC 470 for soils, sediments, and vegetation.<sup>(1)</sup> Studies performed on spiked fish samples indicated that if the TOPO was allowed to equilibrate for several hours after extraction, recovery of uranium from the digest was essentially 100%. The detection limit is  $0.003 \mu\text{g/g}$  for uranium in fish.

The method for methylmercury determination was based on the work of Oda and Ingle.<sup>(4)</sup> This procedure involves the selective reduction of

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inorganic and organic mercury sequentially to mercury vapor in the same sample solution. The mercury vapor is volatilized and determined by cold vapor atomic absorption. Under the experimental conditions, stannous chloride reduces only inorganic mercury to elemental mercury which swept out of the cell and its absorbance measured. Sodium borohydride then reduces the remaining organic mercury in the sample to Hg vapor which is volatilized and determined by Atomic Absorption. It is assumed that all organomercury is present as methylmercury.<sup>(5,6)</sup> No control samples for methylmercury in fish were available at the time of analysis thus recovery studies were based on spiked samples of fish. All methylmercury concentrations are expressed as micrograms Hg per gram of fish rather than  $\mu\text{g}$  methylmercury per gram of fish. The precision of the method based on triplicate analysis of 8 fish samples is  $\pm 0.04 \mu\text{g Hg/g fish}$ . The detection limit has been set at  $0.05 \mu\text{g Hg per gram of fish}$  for a 0.5 g sample.

The development and routine analysis of these samples were directed by "low level" laboratory of the Environmental, Industrial Hygiene and Radiochemical Analysis section. The analysis for PCBs and uranium was carried out in this section also. The methylmercury analysis was performed in the Spectrochemical Analysis section. Please call me if you have any questions or require further evaluation of the data.

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Table 1. Results from Fish Analysis Program

Location (Poplar Creek)	Sample Code	Species	Length (cm)	Weight (gram)	Sex	PCBs as 1260 µg/g Fish	Uranium µg/g Fish	CH <sub>3</sub> Hg <sup>+</sup> as Hg µg/g Fish
PC-1	1	Yellow Bass	16.8	54.5	F	0.1	0.007	0.25
"	2	" "	17.6	65.5	F	<0.1	0.007	0.20
"	3	" "	17.5	63.1	M	0.2	<0.003	0.18
"	4	" "	17.7	65.4	F	<0.1	<0.003	0.09
"	5	" "	16.5	58.6	M	0.1	0.004	0.18
"	6	" "	17.1	62.4	M	0.2	0.010	0.11
"	7	" "	14.0	32.8	M	<0.1	0.012	0.10
"	8	" "	14.1	32.8	F	<0.1	0.011	0.08
"	9	" "	13.0	28.4	M	0.1	0.010	0.06
"	10	" "	13.5	28.5	M	<0.1	0.018	0.09
"	11	Drum	22.6	132.7	M	<0.1	0.007	0.08
"	12	"	16.0	38.7	M	<0.1	0.015	0.07
"	13	Bluegill	15.7	84.7	F	<0.1	0.009	0.07
"	14	"	13.7	54.3	M	<0.1	0.007	0.15
"	15	"	14.7	72.7	M	<0.1	0.007	0.23
"	16	"	12.2	36.0	M	<0.1	0.004	0.32
"	17	"	11.3	31.6	F	<0.1	0.009	0.24
"	18	Striped Bass	14.1	23.0	?	0.2	0.008	0.08
"	19	" "	24.0	153.9	M	<0.1	<0.003	<0.05
"	20	White Bass	29.3	315.4	M	<0.1	0.004	<0.05
"	21	Hybrid	38.7	817.1	M	<0.1	0.005	0.28
"	22	Spotted Bass	13.7	35.7	F	<0.1	<0.003	0.11
"	23	Channel Catfish	51.6	1255.6	?	0.4	<0.003	1.34
PC-2	24	Crappie	17.7	50.3	?	0.4	0.009	0.48
"	25	"	20.0	70.2	M	0.3	0.005	0.55
"	26	"	21.8	98.1	M	0.1	<0.003	0.39
"	27	"	21.6	93.8	F	0.1	<0.003	0.46
"	28	"	20.3	85.9	F	0.2	0.004	0.31
"	29	"	20.3	84.3	F	0.2	<0.003	0.34
"	30	"	22.3	108.2	F	0.4	0.004	0.46
"	31	"	19.5	66.1	F	0.2	0.005	0.35
"	32	"	20.5	81.1	F	0.2	0.006	0.40
"	33	"	34.2	546.6	F	0.2	<0.003	0.63
"	34	Yellow Bass	17.2	56.6	F	0.1	0.010	0.52
"	35	" "	18.9	65.9	F	0.2	0.007	0.42
"	36	" "	16.1	46.1	M	0.3	0.013	0.50
"	37	" "	14.6	33.7	F	0.1	0.019	0.09
"	38	" "	16.0	59.9	F	0.1	0.011	0.35
"	39	" "	14.5	31.8	M	0.3	0.013	0.12
"	40	" "	13.4	25.2	M	0.2	0.017	0.07
"	41	" "	13.7	27.3	M	<0.1	0.009	0.14
"	42	" "	11.8	17.9	M	<0.1	0.012	0.43

Table 1. Results from Fish Analysis Program (continued)

Location (Poplar Creek)	Sample Code	Species	Length (cm)	Weight (gram)	Sex	PCBs as 1260 µg/g Fish	Uranium µg/g Fish	CH <sub>3</sub> Hg <sup>+</sup> as Hg µg/g Fish
PC-2	43	Drum	24.5	165.8	F	<0.1	0.007	0.52
"	44	Sm. Mouth Bass	14.5	29.0	M	<0.1	0.007	0.58
"	45	Lg. Mouth Bass	13.5	25.0	M	<0.1	0.006	0.64
"	46	" " "	22.9	145.8	F	<0.1	<0.003	1.03
"	47	Bluegill	15.4	58.9	M	<0.1	<0.003	0.69
"	48	"	15.6	81.9	F	<0.1	0.004	0.40
"	49	"	14.6	48.9	F	<0.1	0.017	0.50
"	50	"	13.6	39.9	F	<0.1	0.004	0.40
"	51	"	13.1	45.0	M	<0.1	0.006	0.36
"	52	"	12.1	37.8	F	<0.1	<0.003	0.44
"	53	"	12.1	36.8	M	<0.1	0.009	0.42
"	54	"	10.6	19.4	M	<0.1	<0.003	0.45
"	55	"	10.3	18.7	M	0.1	0.009	0.39
"	56	"	9.3	13.2	M	<0.1	INS	0.33
"	91	Blue Catfish	39.6	492.0	F	<0.1	0.008	0.06
"	92	" "	35.4	341.0	M	<0.1	0.009	0.07
"	93	Channel Catfish	44.1	887.0	F	0.5	0.007	1.07
"	94	" "	55.2	225.5	F	0.7	0.004	0.29
"	95	" "	56.1	1750.0	M	0.5	0.005	0.40
"	96	" "	52.7	1539.0	M	0.3	0.008	0.70
PC-3	57	Crappie	21.7	110.5	F	<0.1	<0.003	0.11
"	58	"	23.0	123.1	F	0.2	<0.003	0.48
"	59	"	22.4	104.1	M	<0.1	<0.003	0.17
"	60	"	24.0	138.3	F	<0.1	<0.003	0.37
"	61	"	21.1	93.1	M	<0.1	0.005	0.15
"	62	"	21.8	105.8	M	<0.1	<0.003	0.42
"	63	"	21.6	91.3	M	<0.1	<0.003	0.23
"	64	Bluegill	19.4	158.4	M	<0.1	0.004	0.35
"	65	"	18.5	135.5	M	<0.1	<0.003	0.47
"	66	"	16.7	106.6	M	<0.1	0.004	0.30
"	67	"	18.9	142.3	M	<0.1	0.004	0.52
"	68	"	17.7	110.3	F	<0.1	0.001	0.78
"	69	"	15.8	74.7	F	<0.1	0.004	0.40
"	70	"	14.0	60.5	M	<0.1	0.004	0.28
"	71	"	13.9	54.8	F	<0.1	0.005	0.24
"	72	"	12.2	31.2	F	<0.1	0.015	0.38
"	73	"	11.7	27.8	F	<0.1	0.006	0.21
"	74	Drum	26.2	163.9	M	0.1	<0.003	0.15
"	75	"	21.9	108.6	M	<0.1	<0.003	0.08
"	76	"	20.3	74.2	M	<0.1	0.004	0.30
"	77	Lg. Mouth Bass	25.1	204.8	M	<0.1	0.003	0.43
"	78	" " "	19.0	76.4	M	<0.1	<0.003	0.59
"	79	" " "	14.9	33.2	M	1.0	0.006	0.38

Table 1. Results from Fish Analysis Program (continued)

Location (Poplar Creek)	Sample Code	Species	Length (cm)	Weight (gram)	Sex	PCBs as 1260 $\mu\text{g/g}$ Fish	Uranium $\mu\text{g/g}$ Fish	$\text{CH}_3\text{Hg}^+$ as Hg $\mu\text{g/g}$ Fish
PC-3	80	Sauger	37.5	371.1	M	<0.1	0.003	0.26
"	81	"	44.6	734.6	M	0.2	0.004	0.44
"	82	"	46.9	951.6	F	0.1	0.003	0.70
"	83	"	39.1	484.0	M	0.2	0.025	0.63
"	84	"	38.3	524.1	M	0.2	0.009	0.24
"	85	Blue Catfish	52.7	1313.1	M	0.5	0.007	0.18
"	86	Channel Catfish	31.5	238.2	M	0.1	0.005	0.12
"	87	" "	35.0	352.2	M	0.4	0.013	0.11
"	88	Yellow Catfish	34.8	300.5	M	0.3	0.005	0.06
"	89	" "	47.5	1083.0	M	0.4	0.011	0.15
"	90	" "	37.5	435.2	M	<0.1	0.005	0.11

INS = Insufficient sample

Table 2. Comparison of Reference Values and ORGDP Values for PCBs in Fish Concentrate No. 1<sup>A</sup>

U.S. EPA Reference Value $\mu\text{g/g}$		ORGDP value $\mu\text{g/g}$
PCB 1260	$0.92 \pm 0.36$	$1.4 \pm 0.3^*$
PCB 1254	$3.12 \pm 1.32$	
PCB 1242	$1.12 \pm 0.83$	

\* Average of 12 determinations

A At 95% confidence limit

## REFERENCES

1. Environmental and Effluent Analysis Control Manual, Union Carbide Corporation, Nuclear Division.
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